A simple technique for measuring the fracture energy of lithiated thin-film silicon electrodes at various lithium concentrations

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HIGHLIGHTS
- The fracture energy of lithiated Si was measured at various states of charge.  
- A bending test was performed to determine the critical strain for crack initiation.  
- The elastic modulus decreased from 113 GPa for a-Si to 31.6 GPa for Li3.28Si.  
- The fracture energies were determined to be 12.0 J m−2 (a-Si) and 10.0 J m−2 (Li3.28Si).

ABSTRACT
We have measured the fracture energy of lithiated silicon thin-film electrodes as a function of lithium concentration using a bending test. First, silicon thin-films on copper substrates were lithiated to various states of charge. Then, bending tests were performed by deforming the substrate to a pre-defined shape, producing a variation of the curvature along the length of the electrode. The bending tests allow determination of the critical strains at which cracks initiate in the lithiated silicon. Using the substrate curvature technique, we also measured the elastic moduli and the stresses that develop in the electrodes during electrochemical lithiation. From these measurements, the fracture energy was calculated as a function of lithium concentration using a finite element simulation of fracture of an elastic film on an elastic-plastic substrate. The fracture energy was determined to be $G = 12.0 \pm 3.0$ J m$^{-2}$ for amorphous silicon and $G = 10.0 \pm 3.6$ J m$^{-2}$ for Li3.28Si, with little variation in the fracture energy for intermediate Li concentrations. These results provide a guideline for the practical design of high-capacity lithium ion batteries to avoid fracture. The experimental technique described in this paper also provides a simple means of measuring the fracture energy of brittle thin-films.

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1. Introduction

Lithium ion batteries have been developed to power an increasingly diverse range of applications, such as portable electronic devices and electric vehicles [1–4]. Silicon is considered one of the best candidates as an anode material for the next generation of lithium ion batteries due to its enormous capacity of 3579 mAh g$^{-1}$ (Li15Si4) compared to that of graphite (372 mAh g$^{-1}$), which is currently the anode of choice [5–8]. However, lithium ion insertion and extraction results in a 200–300% increase in volume, which can lead to fracture of the silicon anode during electrochemical cycling [9,10]. Since fracture of the anode can cause a loss of electrical contact and the creation of more surface area for solid electrolyte interphase (SEI) growth, mechanical stability is a key issue in commercial battery applications [11–15].

A number of studies have reported mechanical properties of silicon electrodes. Mönig and colleagues [16,17] investigated the elastic modulus of lithiated silicon nanowires by uniaxial tensile testing. Hertzberg et al. [18] measured the hardness and the elastic modulus of lithiated silicon films using depth-sensing indentation measurements. They found that the hardness decreases from 5 to 1.5 GPa and that the elastic modulus decreases from 92 to 12 GPa in changing from the as-deposited silicon to the fully lithiated silicon (Li15Si4). Also, Sethuraman et al. [19] performed in-situ stress measurements of thin-film silicon electrodes using the substrate-curvature technique, finding a biaxial elastic modulus of 70 GPa.

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for Li0.32Si and 35 GPa for Li3.0Si. Pharr et al. [20] evaluated the fracture energy $\Gamma$ of lithiated silicon by monitoring the stress and morphological development of cracks during electrochemical cycling. They measured a fracture energy of $8.5 \pm 4.3 \text{ J m}^{-2}$ at small concentrations of lithium ($-\text{Li0.5Si}$), and established bounds of $5.4 \pm 2.2 \text{ J m}^{-2}$ to $6.9 \pm 1.9 \text{ J m}^{-2}$ for $\Gamma$ at large concentrations of lithium ($-\text{Li2.8Si}$). In addition, Nadimpalli et al. [21] estimated an upper bound of $9 - 11 \text{ J m}^{-2}$ for the fracture energy of Li0.4Si based on stress data and electron microscopy observations. However, these measurement techniques have limitations due to the difficulty of determining the critical stress at which cracks initiate on the surface of the electrode. Furthermore, experimental measurements of fracture energy over a range of lithium concentrations are lacking. In order to design durable silicon electrodes, it is essential to know the fracture energy as a function of state of charge.

In this study, we introduce a simple technique for measuring the fracture energy of thin-film silicon electrodes as a function of lithium concentration. We first lithiate amorphous silicon (a-Si) thin-film electrodes on copper substrates to different states of charge. We then perform a bending test by deforming the substrate to a pre-defined shape that allows for a variation in the curvature along the length of the sample. After bending, the electrodes are examined using a focused ion beam (FIB) to obtain both the critical strain for crack initiation and the thickness of the electrodes after lithiation. Using the substrate curvature technique, we measure both the elastic modulus of the lithiated silicon and the stress induced by lithiation. Combining these results, we quantify the fracture energy using a fracture mechanics analysis. The simple technique presented here is not only useful for lithiated-silicon thin-film electrodes but is also generally applicable for measuring the fracture energy of thin-films and coatings.

2. Experimental procedures

All electrochemical measurements were performed using a standard three-electrode configuration in a custom-fabricated, hermetic, Teflon cell with a glass window. Both the reference and counter electrodes consisted of lithium foil, while the working electrode was a thin-film of amorphous silicon on a copper substrate (McMaster-Carr, annealed electrolytic tough pitch copper). To fabricate the working electrode, mechanically polished copper substrates ($10 \text{ mm} \times 70 \text{ mm}$) with a thickness of 0.8 mm were electro-polished (2 V, 15 min) in phosphoric acid (85 wt%) and placed in a sputter deposition system (ATC 1800, AJA Int., Scituate). Immediately before deposition, the substrates were plasma cleaned for 5 min in 20 mTorr of argon using an RF power of 24 W. Then, 20 nm of copper was deposited onto the substrates using an argon working pressure of 5 mTorr and a DC power of 200 W. The purpose of this copper film was to provide a fresh surface for silicon film deposition. The silicon film was then deposited directly onto the copper film using an argon pressure of 5 mTorr and a DC power of 100 W. The working area of each silicon electrode was $10 \text{ mm} \times 35 \text{ mm}$, and the silicon electrode thickness was $550 \pm 15 \text{ nm}$.

The electrolyte consisted of a 1 M solution of LiPF6 in 1:1:1 (wt%) ethylene carbonate:diethyl carbonate:dimethyl carbonate. The electrochemical cells were assembled in a glove box in an ultrahigh vacuum chamber. The silicon electrodes were lithiated at a constant current density of $100 \mu\text{A cm}^{-2}$ (a C/18 rate assuming a capacity of 3579 mAh g$^{-1}$), and then potentiostatically held until the current dropped to less than 4% of its original value to reach diffusive equilibrium at four different states of charge: 1/4 (895 mAh g$^{-1}$), 1/2 (1790 mAh g$^{-1}$), 3/4 (2684 mAh g$^{-1}$), and full (3579 mAh g$^{-1}$). All lithiation processes were conducted within a voltage window of 0.05–3.0 V. After lithiation, the electrodes were removed from the cell, rinsed in dimethyl carbonate (DMC), and dried for 5 min inside the glove box.

Bending tests on the working electrodes were performed inside the glove box 15 min after removing the electrodes from the cell. The tests were performed using a Delrin mandrel (Fig. 1a) that consisted of a male and a female part. The female part had the shape of an ellipsoid, described in x-y coordinates by $9x^2 + y^2 = 9$ (cm), to impose a variable curvature along the length of the sample; the male part had a similar shape, accounting for sample thickness. The strain in the surface of the substrate is then given by $[22]$

$$\epsilon = \frac{h_{\text{sub}}}{2r},$$

where $h_{\text{sub}}$ is the thickness of substrate and $r$ is the local radius of curvature of the substrate. The strain imposed on the electrode film is tensile and varies from 11% in the center of the sample to 0.9% at the edge, as illustrated in Fig. 1b. Prior to bending, the silicon electrodes were scratched with a diamond scribe to introduce imperfections with sizes on the order of the film thickness [20]. Also, marks were drawn at 1 mm increments along the specimen to quantify the position of crack initiation. Then, the samples were placed between the male and female parts of the mandrel and deformed to the shape of the mandrel. Two sets of samples were tested under identical conditions to examine the reproducibility of the experiments. The mandrels are quite stiff, which ensures reproducible deformation of the sample as long as it is in full contact with the surfaces of the mandrel. After the bending test, the samples were sealed in an airtight container inside the glove box and immediately transferred to a focused ion beam (FIB, Zeiss Nvision 40) chamber to examine the electrode surfaces. During transfer, the samples were exposed to air for less than 30 s. The elastic modulus of the pure silicon film was measured by performing nano-indentation tests using a Hysitron Tribolab nano-indentation system. Indentation tests were performed in load control at a constant loading rate of 200 $\mu\text{N s}^{-1}$. A total of 25 indentations were made in a $5 \times 5$ array with a spacing of 5 $\mu\text{m}$ between the indentations.

3. Results and discussion

Since the silicon thin-film electrodes are constrained in the plane of the film by the relatively thick substrate, lithium insertion is accommodated entirely by expansion of the electrodes in the thickness direction. Thus, it is reasonable to take the thickness of the film, $h_f$, to be linear in the state of charge,

$$h_f = h_0(1 + \beta s),$$

where $h_0$ is the initial thickness of the film, $\beta$ is related to the atomic volumes ($\Omega$) of silicon and the lithiated phase by $\beta = (\Omega_{\text{Li2.75Si}} - \Omega_s)/\Omega_s = 2.8$ (silicon undergoes a 280% increase in volume when it is fully lithiated), and $s$ is the state of charge of the electrolyte, with a value of 0 representing pure silicon and a value of 1 representing the fully lithiated state (assumed to be Li1.75Si with a capacity of 3579 mAh g$^{-1}$) [20, 23]. It should be noted, however, that SEI formation consumes lithium and thus affects both the thickness of the film and the apparent state of charge [11, 24]. In order to examine the effects of SEI formation, we measured the thickness of Li$_x$Si after different lithiation times using FIB cross-sectioning. Fig. 2 shows the thickness of a Li$_x$Si thin-film as a function of time for a constant charge rate. The initial thickness of the amorphous silicon...
is 550 nm. The black squares represent the expected thicknesses determined using Equation (2) and the state of charge calculated from the lithiation time; the red circles represent the average thicknesses measured by FIB observation. Interestingly, the measured thickness of the silicon electrode is very nearly constant for 2 h and then increases linearly with lithiation time. This observation suggests that most of the lithium inserted during the initial 2 h of the lithiation process was actually used in forming SEI, as opposed to forming the lithiated silicon phase. The observation also suggests that relatively little lithium was used in forming SEI after this initial stage. It is likely that a similar phenomenon occurs in other experimental studies. Thus, this result stresses the need for exercising caution in directly relating the lithiation time to the state of charge in experimental studies. Correspondingly, in this study, we determine the states of charge not from the lithiation time, but based on measurements of the silicon electrode thickness.

The critical strain for fracturing a lithiated silicon electrode can be determined from bending experiments on the electrodes. During bending, small flaws in the lithiated silicon start to grow and propagate in regions where the energy release rate reaches the fracture energy of the lithiated silicon. Thus, the boundary between the cracked and un-cracked regions of the sample provides a measurement of the critical applied strain, \( \varepsilon_c \), for fracture. (Shown in Table 1.) Fig. 3(a)–(c) show surface images of a lithiated silicon sample (Li\(_{1.4}\)Si) after a bending test. The cracks propagate in the transverse direction of the sample, and the crack density near the center of the sample (Fig. 3(a)) is larger than near the edge of the sample (Fig. 3(c)). Fig. 3(d) shows a cross-section of a crack near the boundary between the cracked and un-cracked regions of the sample. Although the sample was lithiated for 8 h, the thickness of the lithiated silicon was 1135 nm, which is approximately 200 nm thinner than the value calculated from Equation (2). This provides clear evidence that lithium is used in the formation of the SEI in the initial lithiation stage. The faces of the cracks appear quite flat and perpendicular to the substrate, suggesting brittle fracture. In addition, the crack opening is quite narrow and there is no evidence of sliding at the interface between the lithiated silicon and copper; any such effects are thereby neglected in these experiments [25,26]. The applied critical strain by itself does not provide sufficient information to evaluate the fracture toughness of the coating. In particular, the energy release rate that drives crack propagation depends on the total stress developed in the film prior to fracture. This total stress can be calculated from the critical bending strain, and from knowledge of the elastic modulus of the film and the stress that develops in the film prior to the bending experiment (i.e., from lithiation).

To determine the elastic modulus and the stress at different states of charge, we performed additional electrochemical experiments using 142 nm silicon films on glass substrates (0.4 mm) as anodes. These anodes contained a 300 nm copper film between the silicon and the substrate as a current collector; 20 nm of titanium was used as an adhesion layer between the substrate and the current collector. Three sets of samples were tested under identical conditions. The stress in the lithiated silicon film was determined by measuring the curvature of the substrate with an in-situ multi-beam optical sensor (K-Space Associates, Inc.) during lithiation/delithiation. Details of the experimental method have been published in a previous paper [20]. The average stress in the film was then deduced from the substrate curvature using Stoney’s equation [20,27,28]:

\[
\sigma = \sigma_r + \frac{E_s h_s^2}{6 h_f (1 - \nu_s)} \Delta K,
\]

where \( \sigma \) is the average stress in the film, \( \sigma_r \) is the residual stress in the as-deposited silicon film, \( E_s \) is the elastic modulus of the substrate, \( h_s \) is the thickness of the substrate, \( \nu_s \) is Poisson’s ratio of the substrate, and \( \Delta K \) is the change in substrate curvature induced by changes in the film stress. The value of the residual stress in the as-

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**Fig. 1.** (a) Photograph of the mandrel used for the bending tests. (b) Calculated strain as a function of the position from the center of the sample.

**Fig. 2.** Thickness of a thin-film silicon electrode as a function of the lithiation time at a constant charge rate of C/16. The initial thickness of the silicon electrode is 550 nm. The black squares are values calculated by FIB cross-section. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
deposited silicon film, \(\sigma_\text{fl} = 45\) MPa, was determined by measuring the curvature of the glass substrate before and after silicon deposition. In the calculations, values of the curvature of the glass substrate before and after silicon deposition, Li1.4Si, Li2.34Si, and Li3.28Si. During these delithiation segments, the elastic modulus of the electrode measuring the change in stress in the electrode, as has been done in previous studies\[19,20\]. The elastic modulus of the lithiated silicon was determined by measuring the electrode thickness measurements. Then, the electrode strongly. Further increases in lithium concentration lead to a more gradual decrease of the stiffness. Previously, Hertzberg et al.\[18\] reported that the elastic modulus decreases from 92 GPa (pure silicon) to 12 GPa (fully lithiated silicon). Furthermore, Sethuraman et al.\[19\] measured an elastic modulus of 51 GPa for Li0.32Si and 26 GPa for Li3.0Si, and Ratchford et al.\[32\] reported an elastic modulus of ~35 GPa for fully lithiated silicon. All previous studies and our work suggest that lithium insertion into silicon causes an elastic softening of silicon. However, the numerical values of the moduli are slightly different among the different experiments, most likely due to the use of a different measurement technique \[18,32\] or reference state \[19\] for calculating the moduli.

Bending tests were performed on the lithiated electrodes

\[
E_f = -3\frac{1 + \nu_s}{\beta} \frac{\Delta \sigma}{\Delta s} (1 - \nu_f),
\]

where \(\nu_f\) is Poisson's ratio of the electrode \[31\] and \(\Delta \sigma / \Delta s\) is the increment of the stress over a sufficiently small change of the state of charge. Our experimental data are designated with red star symbols. The values are averages of three individual experiments; the value for pure amorphous silicon was determined using nanoindentation. Evidently the elastic modulus has decreased significantly at low lithium concentrations \((x = 0.47)\), indicating that even a small amount of lithium affects the properties of the silicon electrode strongly. Further increases in lithium concentration lead to a more gradual decrease of the stiffness. Previously, Hertzberg et al.\[18\] reported that the elastic modulus decreases from 92 GPa (pure silicon) to 12 GPa (fully lithiated silicon). Furthermore, Sethuraman et al.\[19\] measured an elastic modulus of 51 GPa for Li0.32Si and 26 GPa for Li3.0Si, and Ratchford et al.\[32\] reported an elastic modulus of ~35 GPa for fully lithiated silicon. All previous and our work suggest that lithium insertion into silicon causes an elastic softening of silicon. However, the numerical values of the moduli are slightly different among the different experiments, most likely due to the use of a different measurement technique \[18,32\] or reference state \[19\] for calculating the moduli.

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Bending tests were performed on the lithiated electrodes
exactly 15 min after lithiation. Several researchers have reported rapid stress relaxation in silicon electrodes upon current interruption [19,33,34]. As the driving force for fracture scales with the square of the stress (Equation (6)), even a small amount of stress relaxation can affect the calculation of the fracture energy significantly. Therefore, we measured the relaxation stress ($\sigma_{\text{relax}}$) in the electrodes after current interruption. Fig. 5(a) and (b) show representative responses of the potential and stress during lithiation and open-circuit segments for a 142 nm amorphous silicon electrode. As shown in Fig. 5(b), the stress continuously decreases in absolute value during the open-circuit segments. This stress relaxation is quantitatively consistent with previous reports [34] and may be attributed to the high mobility of lithium atoms, which facilitates effective bond switching to accommodate mechanical deformation [35]. The amount of stress relaxation after 15 min of open circuit is plotted in Fig. 5(c).

Fracture of the electrode occurs in the form of long channel cracks in the lithiated silicon film. The energy release rate or driving force for this type of cracks can be calculated using an analysis by Beuth for cracks in a thin-film on an elastic half space [36,37]. Pharr

Fig. 4. Representative responses in (a) potential vs Li/Li$^+$ and (b) stress as a function of lithiation time during a galvanostatic test of a 142 nm amorphous silicon film. (c) Elastic modulus and flow stress after lithiation of the film as a function of lithium concentration.

Fig. 5. Representative responses in (a) potential vs Li/Li$^+$ and (b) stress as a function of lithiation time from a galvanostatic test of a 142 nm amorphous silicon film. (c) Relaxation stress of silicon film after 15 min of open circuit as a function of lithium concentration.
et al. [20] have discussed in detail the validity of such an analysis in this context. However, one concern with Beuth's analysis is the assumption of an elastic substrate, which is clearly violated in our bending experiments on copper substrates. To evaluate the impact of substrate plasticity on the calculation of the fracture energy, we performed finite element analyses of the energy release rate in the presence of substrate plasticity. For the lithiated yield strength of amorphous $\text{Li}_x\text{Si}$ in all of our fracture experiments. The critical stresses to cause fracture were found to be less than the available for fracture of the film, i.e., the energy release rate, is then related to these energies by:

$$G = \frac{2(U_{\text{no-crack}} - U_{\text{crack}})}{h_f},$$

where $h_f$ is the thickness of the film, $U_{\text{no-crack}}$ represents the internal energy of the system just before the crack is introduced, and $U_{\text{crack}}$ represents the internal energy of the system at the end of the simulation. The factor of two in Equation (5) arises since only half of the geometry was simulated. Following standard practice, the pre-factor $Z$ is then calculated through:

$$G = Z\sigma_f^2h_f,E_f,$$

where $\sigma_f$ is the critical total stress in the film to cause cracking, and $E_f = E_f/(1 - \nu_f^2)$ is the plane-strain modulus of the film, where $\nu_f$ is Poisson's ratio of the film.

Combining (5) and (6) yields:

$$Z = \frac{2E_f(U_{\text{no-crack}} - U_{\text{crack}})}{\sigma_f^2h_f^2}.$$  

This approach was verified in ABAQUS by making the substrate elastic and comparing to Beuth's results for a number of geometries and materials constants (results not shown here) [36]. The results from ABAQUS were in agreement with the results obtained by Beuth to within 5–10%. Using this approach, the pre-factor $Z$ was found as a function of the lithium concentration and is tabulated in Table 1.

At the critical bending strain to induce fracture, $G = \Gamma$ and Equation (6) can be used to find the fracture energy. Since the critical bending strains (Table 1) are much larger than the yield strain of Cu (approximately 0.3%), we assume that plastic deformation in the substrate occurs during the entire bending experiment, i.e., effectively, $\nu_s = 0.5$. During bending and prior to fracture, the film is under a state of plane stress. Assuming continuity at the interface between the film and the substrate, the change in stress in
the film due to bending can be found from Hooke’s law:

$$\varepsilon_{11}^{\text{bend}} = \frac{1}{E_1} \left( \sigma_{11}^{\text{bend}} - v_2 \sigma_{22}^{\text{bend}} \right) = \varepsilon_c,$$

(8)

$$\varepsilon_{22}^{\text{bend}} = \frac{1}{E_2} \left( \sigma_{22}^{\text{bend}} - v_1 \sigma_{11}^{\text{bend}} \right) = \varepsilon_c,$$

(9)

where $\varepsilon_c$ is the critical bending strain to cause fracture (Table 1). The subscripts 1 and 2 refer to the directions parallel and perpendicular to the long edge of the sample, respectively.

Combining (8) and (9) gives the bending stress ($\sigma_{b}$):

$$\sigma_b = \varepsilon_c \frac{E_f}{E_f \varepsilon_c + \frac{1 - v_1 v_2}{1 - v_2^2}}.$$

(10)

Using $v_1 = 0.5$, and $v_2$, $E_f$, and $\varepsilon_c$ from Table 1, the critical stress for fracture (summation of $\sigma_{b}$, $\sigma_{\text{flow}}$, and $\sigma_{\text{relax}}$) is calculated from Equation (10) and is listed in Table 1. With the critical stress known, we can use Equation (6) to calculate the fracture energy – the results are shown in Table 1 and Fig. 7. The fracture energy of the pure silicon film is $\Gamma = 12.0 \pm 3.0$ J m$^{-2}$. Although the lithium concentration of the electrode increases to Li$_{3.28}$Si, the fracture energy remains similar ($\Gamma = 10.0 \pm 3.6$ J m$^{-2}$) to that of pure silicon. These fracture energies are quite typical for brittle solids, in agreement with the observation of brittle fracture morphologies in the bending experiments (Fig. 3). The values of the fracture energy do not change much with lithium concentration, even though the stiffness of the coatings changes dramatically. The one exception is the fracture energy of Li$_{0.47}$Si, which is significantly lower than the other values. Part of this reduction may be explained by a decrease in the stress measurement. In particular, the stresses measured may be inaccurate at these small lithium concentrations because the stress state varies rapidly at the onset of lithiation. However, the error in the stress measurement alone is not sufficient to explain the low value of the fracture energy and it is possible that the fracture energy goes through a minimum near this lithium concentration. Previously, Pharr et al. [20] have reported a fracture energy for lithiated silicon of $8.5 \pm 4.3$ J m$^{-2}$ at low concentrations of lithium (Li$_{2.5}$Si), and established bounds of $5.4 \pm 2.2$ J m$^{-2}$ to $6.9 \pm 1.9$ J m$^{-2}$ at large concentrations of lithium (Li$_{2.3}$Si). These values are in reasonable agreement with the fracture energies measured in this study: $9.2 \pm 3.3$ J m$^{-2}$ at Li$_{1.4}$Si and $10.8 \pm 1.9$ J m$^{-2}$ at Li$_{3.34}$Si. The small discrepancy may be caused by the history dependence of the plastic flow that occurs in the substrate during crack growth: As the crack propagates, the precise strain history in the ABAQUS model may be slightly different from the actual strain history. The energy dissipated in the substrate during crack growth is then slightly different from the calculated value, leading to a small error in the energy release rate calculated by ABAQUS.

The technique for measuring fracture energy described in this paper offers a number of important advantages over existing techniques. Since the critical bending strain at which the crack initiates is readily determined after the experiment by optical or electron microscopy, more accurate values of fracture energy can be obtained as compared to other techniques [20,21]. Also, customizing the shape of the mandrel allows for a variation in the curvature along the length of the sample that can be prescribed by the user, thereby providing a means of controlling the range of the applied strain. Thus, it is possible to observe a large range of prescribed strains from a single experiment.

4. Conclusion

In this paper, we have determined the fracture energy of lithiated silicon thin-film electrodes at various states of charge. To do so, we performed a simple bending test by deforming the substrate to a customized shape. The states of charge were determined by measuring the thickness of the lithiated silicon electrode, since most of the lithium inserted during the initial stage of the experiment was consumed in forming SEI. Using the substrate curvature technique, the elastic moduli of the electrodes were calculated as a function of lithium concentration, varying from 113 GPa for amorphous silicon to 316 GPa for Li$_{3.28}$Si. In addition, the total critical stress for fracture in the silicon electrodes was found by measuring stresses due to lithiation, relaxation, and bending. From this total critical stress, we quantified the fracture energy through simulations in ABAQUS of an elastic film on an elastic–plastic substrate. The fracture energies were determined to be $\Gamma = 12.0 \pm 3.0$ J m$^{-2}$ for amorphous silicon and $\Gamma = 10.0 \pm 3.6$ J m$^{-2}$ for Li$_{3.28}$Si, with little variation in the fracture energy for intermediate Li concentrations. We believe that the simple technique presented here will be useful for measuring the fracture energy of a wide range of thin-films and coatings.

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Fig. 7. Fracture energy as a function of lithium concentration calculated from Equation (6).
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